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Producing Free Nitrous Acid - A Green and Renewable Biocidal Agent - from Anaerobic Digester Liquor

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Abstract

Recent studies have shown that free nitrous acid (FNA) at parts per million is strongly biocidal to a broad range of microorganisms involved in wastewater management. Applications have been developed, where FNA is used to deactivate anaerobic sewer biofilms thus suppressing sulfide and methane production in sewers, or to lyse secondary sludge resulting in reduced sludge production and enhanced biogas production. This study examines the feasibility of producing FNA from a waste stream namely the anaerobic sludge digestion liquor, thus providing a source of FNA for the above applications within wastewater systems. Complete nitrification was achieved in a lab scale sequencing batch reactor (SBR) treating reject wastewater. Under stable operation, the system sustained more than 90% conversion of the 1.0 and 0.8 g NH₄⁺-N/L contained in the synthetic and real digester liquor, respectively, to nitrite. Each liter of this nitrite rich effluent

could be acidified to pH 2 with only 66 mmole of H^+ , due to the low level of alkalinity in the effluent. This converts almost all of the nitrite to FNA providing an ample source of FNA for sewer and sludge pretreatment applications. Despite the high nitrite concentration in the reactor, minimal N_2O was produced with an emission factor of 0.08% of the ammonium nitrogen converted. Finally, an economical assessment of a theoretical full-scale installation for FNA production was conducted and compared with the costs of producing this FNA from a commercial nitrite supply.

Keywords: Free nitrous acid (FNA); Anaerobic digester liquor; Biocide; Nitrification; Nitrous oxide.

1. Introduction

The protonated form of nitrite, free nitrous acid (FNA), is a metabolic inhibitor to a broad range of microorganisms involved in wastewater treatment systems [1]. It has been reported that, at parts per billion (ppb) levels, FNA has inhibitory effects on: 1) the anabolic and catabolic activities of ammonia and nitrite oxidising bacteria [2, 3]; 2) growth, nitrate and nitrite reduction activities of denitrifying bacteria in activated sludge [4] and 3) aerobic and anoxic phosphorus uptake by polyphosphate accumulating organisms [5, 6]. In addition, FNA has also been shown to inhibit methanogens [7], pathogens [8] and yeast [9]. The demonstrated inhibitory effects of FNA on bacterial cultures cultivated in wastewater systems indicate impending potential of FNA as an agent for manipulating microbial community in wastewater systems.

More recently, it was found that FNA, at parts per million (ppm) or even sub-ppm levels, is strongly biocidal to microorganisms in wastewater systems [10, 11]. FNA dosing at 0.2 – 0.3 mg HNO_2 -N/L for 12 to 24 hours was shown to be able to suppress hydrogen sulfide and methane

formation in anaerobic sewers for several days to weeks [10, 12, 13]. Field trials in real sewers confirmed these results [14] and cell viability tests revealed that FNA treatment of sewer biofilms incurred a substantial loss (85-95%) of cell viability [10]. Pijuan et al. [11] applied FNA to treat secondary activated sludge and observed that FNA at 1-2 mg $\text{HNO}_2\text{-N/L}$ entirely deactivated secondary sludge and was able to significantly improved its biodegradability.

Long-term application of FNA dosing to either sewer biofilm control or secondary sludge treatment will however require a substantial amount of FNA (both nitrite and acid), incurring significant costs and also adding nitrogen load to the treatment plant. One of the plausible ways to address these issues is to recover FNA from nitrogen rich waste streams within the wastewater treatment train, such the anaerobic digester supernatant. Digester liquor contains high concentrations of ammonium in the range of 0.5 – 1.5 g $\text{NH}_4^+\text{-N/L}$. It also contains bicarbonate at a molar ratio to ammonium of approximately 1:1, which provide adequate alkalinity for the conversion of 50% of the ammonium to nitrite by ammonia-oxidising bacteria (AOB) [15, 16]. This stream is currently being treated either by returning it to the mainstream bioreactor or by a side-stream treatment process. In side-stream processes, partial ammonium conversion to nitrite in a nitrification system coupled to anammox process or heterotrophic denitrification is often used in full-scale application [17, 18]. However, the nitrification system can also be adapted to perform complete ammonium oxidation producing an effluent stream predominantly consisting of nitrite [19].

To achieve complete ammonium conversion to nitrite, sufficient alkalinity has to be supplemented with a molar ratio of bicarbonate to ammonium of 2:1. Due to the consumption of bicarbonate during ammonium conversion, the nitrite rich effluent is expected to have relatively low buffering capacity and can be converted to FNA with minimal acid addition. The primary

aim of this study is to demonstrate the feasibility of producing FNA at ppm levels through the nitrification process of reject wastewater. For that a suitable manner to provide the alkalinity required was assessed so that there was a minimal amount of residual alkalinity at the completion of the conversion of ammonium to nitrite. The N_2O emissions for this process were also evaluated as the high-level presence of nitrite could potentially stimulate N_2O production. Finally, an economic analysis was conducted to compare the costs of producing FNA from reject wastewater to the cost associated when using commercial nitrite.

2. Materials and Methods

2.1. Reactor Startup and Operation

An enriched AOB population was cultivated in a sequencing batch reactor (SBR) with a working volume of 8 L to achieve complete ammonium conversion to nitrite. The reactor was seeded with the return activated sludge collected from the Luggage Point wastewater treatment plant (WWTP), Brisbane, Australia. The SBR was operated in identical cycles of 8 hours. Each cycle comprised the following phases in sequence: 2.5 min feeding I (aeration on), 218 min aerobic phase I, 2.5 min feeding II (aeration on), 219.5 min aerobic phase II, 2.5 min of sludge withdrawn (aeration on), 30 min settling and 5 min decanting. In each feeding period, synthetic wastewater (composition described below) of 1 L was added. This resulted in a hydraulic retention time (HRT) of 1.33 days. Dissolved oxygen (DO) concentration was maintained between 2.5 to 3.5 mg O_2/L controlled automatically using an on-off controller. When N_2O was monitored, a constant gas flow was provided to allow a correct calculation of the N_2O emitted. In these cases, a gas mixture of nitrogen and air was used. The nitrogen flow and air flow were adjusted using two mass flow controllers (Smart-Track 50 series, Sierra). The total gas flow rate

of the nitrogen and air mixture entering the reactor was maintained at a fixed rate of 0.65 ± 0.05 L/min. This resulted in less variations on the DO profile compared with the cycles where N_2O was not monitored. In all cases, DO concentration was continuously monitored with an oxygen probe (YSI 5739) connected to a miniCHEM-DO₂ metre. A water jacket was connected to maintain the SBR temperature at 30 ± 1 °C mimicking the typical temperature of digester liquor.

Synthetic wastewater with characteristics of anaerobic digester liquor was used as feed in the first 170 days. The use of synthetic digester liquor for the initial startup phase enabled the ammonium content and ammonium to bicarbonate ratio in the feed to be adjusted according to the ammonia oxidation activity of the biomass. From day 171 onwards, the SBR was fed with real sludge digester liquor. The composition of the synthetic wastewater (modified from Kuai and Verstraete [15]) was: 2.81 – 5.62 g/L of NH_4HCO_3 (0.5 – 1.0 g NH_4^+ -N/L), varied as described below to adjust the nitrogen load to the reactor, 0.064 g/L of each of KH_2PO_4 and K_2HPO_4 and 2 mL of a trace element stock solution. The trace element stock solution contained: 1.25 g/L EDTA, 0.55 g/L $ZnSO_4 \cdot 7H_2O$, 0.40 g/L $CoCl_2 \cdot 6H_2O$, 1.275 g/L $MnCl_2 \cdot 4H_2O$, 0.40 g/L $CuSO_4 \cdot 5H_2O$, 0.05 g/L $Na_2MoO_4 \cdot 2H_2O$, 1.375 g/L $CaCl_2 \cdot 2H_2O$, 1.25 g/L $FeCl_3 \cdot 6H_2O$ and 44.4 g/L $MgSO_4 \cdot 7H_2O$.

The real sludge digester liquor was collected from Luggage Point WWTP on a weekly basis and the main characteristics were: 649 ± 11.6 mg COD/L, 110 ± 3.5 mg PO_4^{3-} -P/L, 822 ± 12.3 mg NH_4^+ -N/L, 7.3 ± 0.4 mg NO_2^- -N/L, 2.5 ± 0.2 mg NO_3^- -N/L and 1.76 ± 0.06 g HCO_3^- /L. The operational conditions applied to the SBR during the startup (Period I), transient (Period II), stable operation (Period III) and real digester liquor (Period IV) phases are summarised in Table 1.

From Day 1 to Day 35, the daily nitrogen load was $0.375 \text{ kg N/m}^3/\text{day}$. In order to wash out NOB rapidly, a short solid retention time (SRT) of 2.67 days was initially applied. On Day 29, when nitrite accumulated to a level that was approximately 50% of the total ammonium conversion, SRT was increased to 11 days to increase the AOB biomass concentration. In this period (Day 1 to Day 35), an additional amount of NaHCO_3 was added to the feed to achieve a 2:1 molar ratio of bicarbonate to ammonium. The resulting pH of the feed was 8.5 ± 0.1 . This ratio provides sufficient alkalinity for the full oxidation of ammonium. pH in the reactor was measured continuously with a pH probe (TPS) connected to a miniCHEM-pH metre, but not controlled.

On Day 36, complete ammonium to nitrite conversion was established. In the following two weeks (Day 36 to Day 49), the nitrogen load of the SBR was gradually increased to $0.563 \text{ kg NH}_4^+-\text{N/m}^3/\text{day}$. In this period, the bicarbonate to ammonium molar ratio in the feed was decreased to 1.5:1. The resulting pH in the feed was 8.5 ± 0.1 . This ratio would not allow full oxidation of ammonium, and therefore additional alkalinity was provided through an on-line pH controller, to enable complete nitrification. A NaHCO_3 solution at a concentration of 1 M was added when pH dropped below a predetermined pH set-point of 6.8. While this approach is more complicated than the method used in the startup period for the provision of alkalinity, it avoids over-dosing of bicarbonate. In addition, a pH set-point of 6.8 was selected to allow gradual adaptation of the biomass to the increase in FNA levels.

On Day 50, the ammonium loading rate was further increased to $0.750 \text{ kg NH}_4^+-\text{N/m}^3/\text{day}$, the designed final loading rate. Similar to the previous period, the bicarbonate to ammonium molar ratio in the feed was 1.5:1, with additional NaHCO_3 provided through the pH controller. Different from the previous period, the pH set-point was lowered to 6.2. A lower pH set-point is

preferred as it further reduces the residual alkalinity in the reactor effluent, thus requiring less acid addition for the production of FNA from nitrite (see Section 2.3). The SBR was operated in the same conditions until Day 170.

From Day 171 to Day 200, the synthetic wastewater was replaced by real digestion liquor. The reactor was operated identically to the previous period.

2.2. Reactor Monitoring

Cycle studies were performed either weekly, when the reactor was fed with synthetic wastewater, or every second day when fed with real wastewater. Mixed liquor samples were taken using a syringe with a sampling interval of 15 to 30 min throughout the 8 h cycle and immediately filtered through disposable Milipore filters (0.22 μ m pore size). The ammonium, nitrite and nitrate concentrations were analyzed using a Lachat QuikChem8000 Flow Injection Analyzer (Lachat Instrument, Milwaukee). The mixed liquor suspended solids (MLSS) concentration and its volatile fraction (MLVSS) were monitored once a week according to the standard methods. pH and DO in the reactor were monitored and controlled on-line as described in 2.1. The FNA concentration was calculated according to Anthonisen et al. [20], using the

formula $\frac{S_{N-NO_2}}{K_a * 10^{pH}}$ and K_a value was found from $e^{-2300/(273+^0C)}$. When N_2O was monitored, the

SBR was sealed with a lid equipped with an off-gas sampling port. The off gas was connected to a URAS 26 infrared photometer (Advance Optima Continuous Gas Analyser AO2020 series, ABB) to measure the N_2O concentration continuously with data logging every 3 sec. Details of the operation and calibration of the analyser are explained in detail in Law et al. [21].

2.3. Acid Titration of the SBR Effluent

After stable operation was achieved in Period III, two acid titration tests were carried out on the treated digester liquor. SBR effluent (0.3 L) was collected and placed in a beaker with a pH

probe (Metrohm Swiss, 827 pH Lab) to record pH. Once the pH reading stabilised, the SBR effluent was titrated with 0.5 M of sulfuric acid. The amount of acid added for each pH change was recorded until the pH reached 2.0. The amount of H^+ added was then calculated based on the amount of sulfuric acid added.

2.4. Microbial Characterisation

The method described by Daims et al. [22] was used to prepare the biomass samples for Fluorescence in situ Hybridization (FISH) analysis. The following probes were used: NEU, specific for *Nitrosomonas* sp.; NSO190 and NSO1225, specific for Betaproteobacterial AOB, Nsv443, specific for *Nitrospira* spp.; Ntspa662, specific for the *Nitrospira* genera and EUB-mix (EUB338, EUB338-II, and EUB338-III), covering most bacteria. All probes were either labeled with 5'FITC, or one of the sulfoindocyanine dyes, indocarbocyanine (Cy3) or indodibocyanine (Cy5). FISH-probed samples were visualised using a Zeiss LSM 510 Meta confocal laser scanning microscope (Carl Zeiss, Jena, Germany) and images were collected using a Zeiss Neofluar $\times 40/1.3$ oil objective. FISH images were analysed using DAIME version 1.3, to determine the biovolume fraction of the bacteria of interest [22].

3. Results and Discussion

3.1. Complete Nitritation for FNA production

Figure 1 shows the influent and effluent ammonium and the nitrite, nitrate and free nitrous acid effluent concentrations over the four experimental periods, initially with synthetic and then with real digester liquor. Ammonium oxidation activity commenced after 10 days from startup and gradually increased with nitrite as the main final product of the conversion. Full conversion of ammonium to nitrite was achieved from Day 42 onwards. The MLVSS concentration

increased gradually, reaching 1.5 g/L on day 133 and kept around 1.3 g/L during the real wastewater test period. The reactor performance was maintained despite an increase in the ammonium concentration in the feed from 500 to 750 mg NH_4^+ -N/L between Day 36 and Day 49, and to 1g NH_4^+ -N/L from Day 50 onwards. More than 90% of the ammonium fed was converted to nitrite, while less than 5% of the loaded ammonium was oxidised to nitrate. On Day 171, the feed was switched to the real digester liquor containing 822 ± 12.3 mg NH_4^+ -N/L. After 5 days of operation, the reactor achieved steady performance with more than 92% ammonium conversion to nitrite. The effluent nitrite concentration was consistently above 760 mg N/L and the FNA concentration was around 1 mg HNO_2 -N/L.

The nitrite rich effluent from the SBR could be further converted to FNA through acidification. Titration of the treated effluent confirmed that the treated digester liquor had a low buffering capacity. The pH of 0.3 liters of effluent could be reduced to 2.0 with the addition of 19.8 ± 0.2 mmole H^+ (Figure 2), corresponding to 66 ± 0.2 mmole H^+ per liter. The amount of nitrite present in the effluent at the time of titration was 67 mM (935 mg N/L). This matches the amount of H^+ consumption, confirming that nitrite was the main buffer present in the effluent. Given that the pKa value of FNA is approximately 3.4 under standard conditions, the pH decreased sharply in the pH range of 6.0-4.0 but more slowly in the range of 4.0-3.0 (Figure 2). The low acid requirement to reduce the effluent pH indicates that high FNA concentrations could be produced at a minimal dosage of acid from the treated digester liquor.

3.2. Performance of the pH controller

The pH controller was crucial in ensuring complete conversion of ammonium to nitrite. In a typical cycle study shown in Figure 3-top, pH increased to approximately 7.8 ± 0.1 after feeding due to the additional alkalinity supplemented in the feed with a bicarbonate to ammonium molar

ratio of 1.5:1. However, the pH in the reactor decreased as the bicarbonate in the feed was consumed. With a 1:1.5 molar ratio of ammonium to bicarbonate, additional bicarbonate requirement was supplemented through the pH controller. The pH set-point of 6.2 enabled the bicarbonate to be supplied only when required. As shown in the titration curve, there was no indication of residual bicarbonate since no buffering capacity was observed at the pH range of 6.0-4.0 (Figure 2). While the ammonium oxidation rate was also slowed down at this low pH (Figure 3), likely due to the low bicarbonate availability [23] or possibly due to partial inhibition by FNA [2, 24], complete nitrification was still achieved with the gradual bicarbonate dosing used in this study.

3.3. Nitrous Oxide Production during Complete Ammonium Conversion to Nitrite

During a typical SBR cycle, an abrupt increase in the N_2O emission (up to 40 ppm v) was observed at the beginning of the first aerobic phase (Figure 4). Such an N_2O spike has been previously observed in lab-scale nitrification systems [25, 26], and is a result of stripping of dissolved N_2O accumulated during the non-aerated settling and decanting phases. The N_2O spike was therefore not observed in the second aerobic phase. The fluctuations in pH and DO concentration did not have an apparent effect on the N_2O production. The N_2O production stayed low throughout the aerobic phases as indicated by the low N_2O emissions detected (≈ 1 ppm v). Despite high concentrations of nitrite of approximately 0.8-1 g NO_2^- -N/L in the SBR, only 0.08% of N converted was emitted as N_2O . The N_2O emission factor is at the lower end of that for full-scale domestic wastewater treatment plant which varies between 0.01-2.9% of N load converted to N_2O [27]. This contradicts previous studies that have shown high N_2O emissions with increasing nitrite concentrations [28]. However, the results support the findings by Law et al. [29] which showed the lowest N_2O production rate by an enriched AOB culture at nitrite

concentrations of 0.5-1.0 g NO_2^- -N/L. It was postulated that the high nitrite concentration inhibits the nitrifier denitrification pathway, a key N_2O production pathway of AOB.

3.4. Key Selection Pressure against NOB

The biomass composition determined using FISH analysis confirmed that $81 \pm 3\%$ of the bacterial population was ammonia oxidizing *beta-proteobacteria* consisting of *Nitrosospira*, *Nitrosococcus* and *Nitrosomonas* species (covered by the NSO190 probe) (Figure 5a). In addition, *Nitrosomonas sp.* most likely dominated the AOB populations with $67 \pm 7\%$ of the EUBMix probe targeted cells also bound to the NEU probe (Figure 5b). There was no signal observed from all of the NOB probes applied. This coincided with the minimal nitrite oxidation activity in the SBR.

The NOB activity in the SBR was successfully maintained at low levels from the initial startup phase and throughout the stable operation phase. This was likely achieved through a combination of several process conditions applied. AOB and NOB have been reported to have a minimum doubling times of 7-8 hours and 10-13 hours, respectively [30]. A short SRT of 2.67 days fixed from Day 1 to Day 29 allowed selective retention of AOB in the inoculated mixed culture sludge while washing out the majority of NOB in the SBR. A short SRT of 1 to 2.5 days has also been suggested to minimise NOB activity in full scale partial nitrification operation [17].

When the SRT was increased to 11 days to build up a higher AOB concentration from Day 29 onwards, pH was a likely crucial factor in maintaining the NOB activity at low levels. The relatively high pH at the beginning of each aerobic phase resulted in a free ammonia (FA) concentration of 6.8 to 7.6 mg NH_3 -N/ L. Vadivelu et al. [31] has shown that *Nitrobacter*, a well-known NOB, will most likely cease to grow at FA concentration above 6.0 mg NH_3 -N/L. Conversely, AOB has been shown to have a maximum oxygen uptake rate at a pH range of 7.0-

7.7 despite a relatively high FA concentration ranging between 6-35 mg $\text{NH}_3\text{-N/L}$ in a nitrification system [23].

In addition the pH set-point also governs the FNA concentration in the SBR. A slight increase in nitrate concentration was observed when the pH set-point was at 6.8 (Day 36 to 49). The nitrate concentration subsequently decreased when the pH set-point was decreased to 6.2 (Day 50 onwards) (Figure 1). The prolonged low pH (6.2 ± 0.1) condition in the SBR (Figure 3) resulted in a relatively high FNA concentration of 1 ± 0.1 mg $\text{HNO}_2\text{-N/L}$. FNA has been demonstrated to initiate inhibition on the anabolic process of *Nitrobacter* at 0.11 mg $\text{HNO}_2\text{-N/L}$ and cease biomass production at concentration as low as 0.023 mg $\text{HNO}_2\text{-N/L}$ [2]. Despite relatively high DO concentrations in the reactor (~ 3.0 mg $\text{O}_2\text{/L}$), there was minimal nitrite conversion to nitrate potentially from FNA inhibition (Figure 3).

3.5. Economic Assessment for FNA production

It is estimated that a maximum of 15-20% of the total nitrogen loading to the treatment plant can be recovered in the form of FNA from nitrification of digester liquor [32]. This represents an ample supply of renewable FNA that could be applied onsite for sludge treatment [33, 34] or transported upstream for sewer applications [14].

This study proved that complete ammonium conversion to nitrite can be sustained to produce FNA in large quantities at relatively low cost from wastewater. Based on the experimental results acquired and key operating parameters applied, an economic assessment of nitrite production using anaerobic digestion liquor was conducted by a desktop scaling-up study for a full-scale WWTP with an influent flow rate of 100,000 $\text{m}^3\text{/d}$, a flow rate of anaerobic digestion liquor of 1,000 $\text{m}^3\text{/d}$ (i.e. 1% of the influent flow, [17]) and a $\text{NH}_4^+\text{-N}$ concentration of 820 mg N/L in the anaerobic digestion liquor. The nitrite production cost was then compared to the price

of commercial supply, as summarized in Table 2. The analysis indicates that annualised total cost of nitrite production would be around \$87,600 lower in comparison with the commercial supply (14% savings), indicating nitrite production using anaerobic digestion liquor as a cost-effective method. In addition, there is a strong environmental incentive for the option of in-situ nitrite production as it avoids adding external chemicals to the sludge and does not lead to a higher N_2O emission in comparison with the case of commercial supply.

3.6. Potential Applications of FNA as a Biocidal Agent for Wastewater Management

One of the key potential applications of FNA is to eradicate unwanted biofilms on the surfaces of wastewater infrastructure and facilities. In anaerobic sewer systems, sulfate reducing bacteria (SRB) and methanogenic archaea from biofilm result in the production of hydrogen sulfide and methane, respectively. Hydrogen sulfide is a hazardous gas that causes corrosion and malodor problems [35]. Methane is a potent greenhouse gas and can contribute significantly to the carbon footprint of wastewater systems [36]. In practice, chemical dosing is used to oxidise or precipitate sulfide, to reduce liquid-gas sulfide transfer, or to reduce SRB and methanogenic activities thus minimising their production [37]. Such strategies require intensive energy input and/or significant amounts of chemicals, and often only targets the symptoms rather than eliminating the biofilm. Due to the potency of FNA as a biocidal agent, 12-hr dosage of FNA at concentrations of 0.2–0.3 mg HNO_2 -N/L every five days can effectively decrease the sulfide production and emission in sewer systems by over 80% [13, 14]. This can substantially reduce the amount of chemicals required compared to conventionally used chemicals such as oxygen, nitrate, ferric/ferrous salts and magnesium hydroxide, which need to be added continuously rather than intermittently. In addition, the FNA dosed can be degraded in downstream treatment processes, as after dilution FNA is biodegradable. Indeed, economic analysis showed that

intermittent FNA dosage is more cost-effective than any other chemicals that are commonly used in sewers for the control of sulfide and methane production [13].

The biocidal property of FNA could also be applied to enhance the biodegradability of secondary activated sludge, thereby achieving sludge reduction in the wastewater treatment line and improving anaerobic digestion in the sludge treatment line. Wang et al. [33] achieved a sludge reduction of 28% in a reactor fed with synthetic wastewater by treating 50% of the secondary activated sludge at an FNA level of 2.0 mg $\text{HNO}_2\text{-N/L}$ for 24 h, and then recirculating the FNA-treated sludge to the reactor for further degradation. Using biochemical methane potential tests, Wang et al. [33] demonstrated that the anaerobic hydrolysis rate and degradation extent of a full-scale secondary activated sludge with FNA pretreatment at 1.78 - 2.13 mg $\text{HNO}_2\text{-N/L}$ for 24 h were improved by approximately 50% (from 0.16 to 0.25 d^{-1}) and 30% (from 0.33 to 0.43), respectively, in comparison with the waste activated sludge without FNA pretreatment.

4. Conclusions

This manuscript demonstrates that FNA can be produced at the desired concentrations from digester liquor through complete conversion of ammonium to nitrite with alkalinity addition. The controlled alkalinity addition ensured full oxidation of ammonium to nitrite and also minimal residual alkalinity in the effluent. The latter supports the conversion of nitrite to FNA with minimal acid addition (66 mmole of H^+ addition per L of effluent). The process has a very low N_2O emission factor ($< 0.1\%$ of N converted). While the overall production cost of FNA is comparable to that supplied commercially, recovering FNA from wastewater is desirable from an environmental perspective.

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Table 1. Operational conditions applied during different periods of the SBR operation.

Period	Days	Molar Ratio of HCO_3^- to NH_4^+ in feed	SRT (days)	N Load (kg N/m ³ /day)	pH of feed (± 0.1)	pH control set-point	Wastewater
I	1-35	2:1	2.67-11	0.375	8.5	N/A	Synthetic
II	36-49	1.5:1	11	0.563	8.1	6.8 then 6.2	Synthetic
III	50-170	1.5:1	11	0.750	8.1	6.2	Synthetic
IV	171-200	1.5:1	11	0.750	8.0	6.2	Real

Table 2. Economic analysis of commercial nitrite supply and nitrite production using anaerobic digestion liquor.

Option	Parameter	Value
Commercial nitrite supply	Period over which capital costs are annualised (i.e. Lifetime) (year)	20
	Interest applied for initial capital expenditure	8.5%
	Price of NaNO ₂ (\$/tonne) ^a	450
	Capital cost of NaNO ₂ storage reactor (including major equipment such as pumps) (\$) ^b	83,000
	Annual cost of NaNO ₂ storage reactor (\$/y)	8770
	Annual NO ₂ ⁻ -N production (tonne/y)	280
	Annual cost of NaNO ₂ (\$/y)	621,600
	Annualised total cost (\$/y)	630,370
Nitrite production using anaerobic digestion liquor	Flow rate of the anaerobic digestion liquor (m ³ /d)	1,000
	NH ₄ ⁺ -N concentration in the anaerobic digestion liquor (mg N/L)	820

Biodegradable COD (bCOD) concentration in the anaerobic digestion liquor (mg/L) ^c	300
HCO ₃ ⁻ /NH ₄ ⁺ -N in the anaerobic digestion liquor (mol/mol)	1
SRT in the FNA production reactor (d)	15
HRT in the FNA production reactor (d)	1.33
Conversion efficiency of NH ₄ ⁺ -N to NO ₂ ⁻ -N	93%
Conversion efficiency of NH ₄ ⁺ -N to NO ₃ ⁻ -N	3%
Period over which capital costs are annualised (i.e. Lifetime) (year)	20
Interest applied for initial capital expenditure	8.5%
Power requirement for NH ₄ ⁺ -N and bCOD oxidation (kwh/kg O ₂)	0.66
Mixing energy in the reactor (kwh/(m ³ ·d))	0.12
Power price (\$/kwh)	0.12
Price of NaHCO ₃ (\$/tonne) ^a	145
Storage time of NaHCO ₃ (d)	10
Volume of FNA production reactor (m ³)	1,400
Capital cost of FNA production reactor (including major equipment such as pumps and air compressor) (\$) ^b	628,950
Annualised cost of FNA production reactor (\$/y)	66,500
Annualised mixing cost of FNA production reactor (\$/y)	7,300
Annualised power cost for the oxidation of NH ₄ ⁺ -N and	87,350

bCOD (\$/y)	
Annual cost of NaHCO ₃ (\$/y)	240,000
Volume of NaHCO ₃ storage reactor (m ³)	530
Capital cost of NaHCO ₃ storage reactor (including major equipment such as pumps) (\$) ^a	312,000
Annualised cost of NaHCO ₃ storage reactor (\$/y)	33,000
Annual NO ₂ ⁻ -N production (tonne/y)	280
Annualised total cost (\$/y)	717,950
Annual saving (\$/y)	87,580
Annual saving (%)	14%

^a<http://www.alibaba.com/>

^bThe capital cost of the reactor was estimated using the following equation [38]:

$493601 \times (V/1000)^{0.7202}$, where V=volume of the bioreactor

^cbased on the characteristics of the real digester liquor reported in this study, and assuming bCOD/COD=0.45

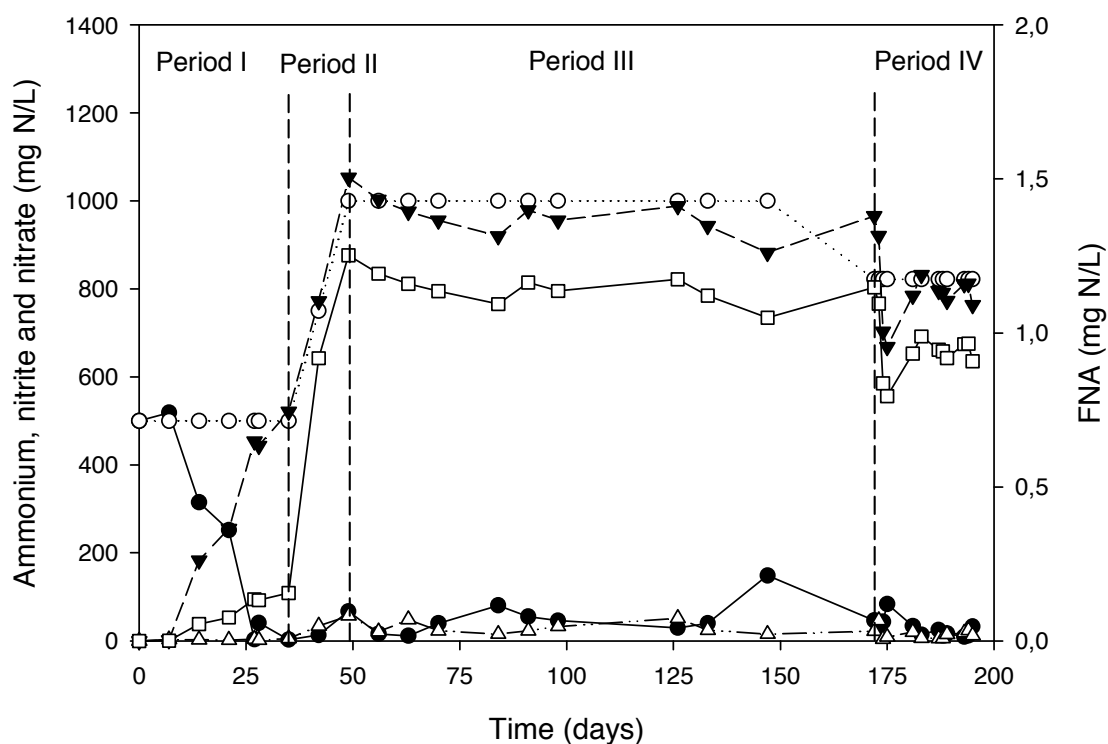


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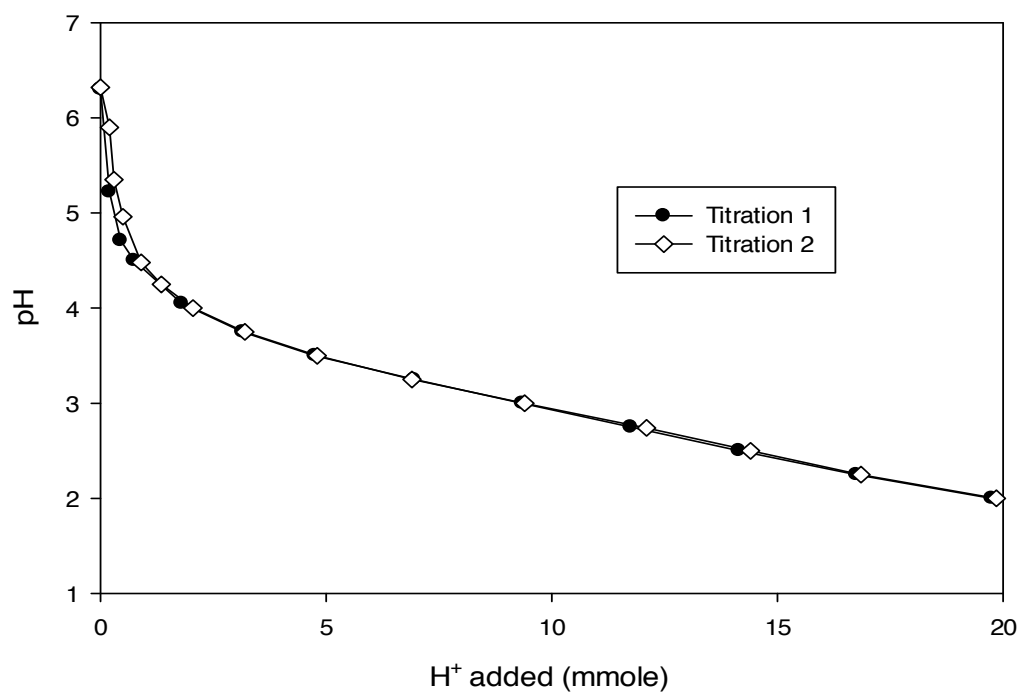


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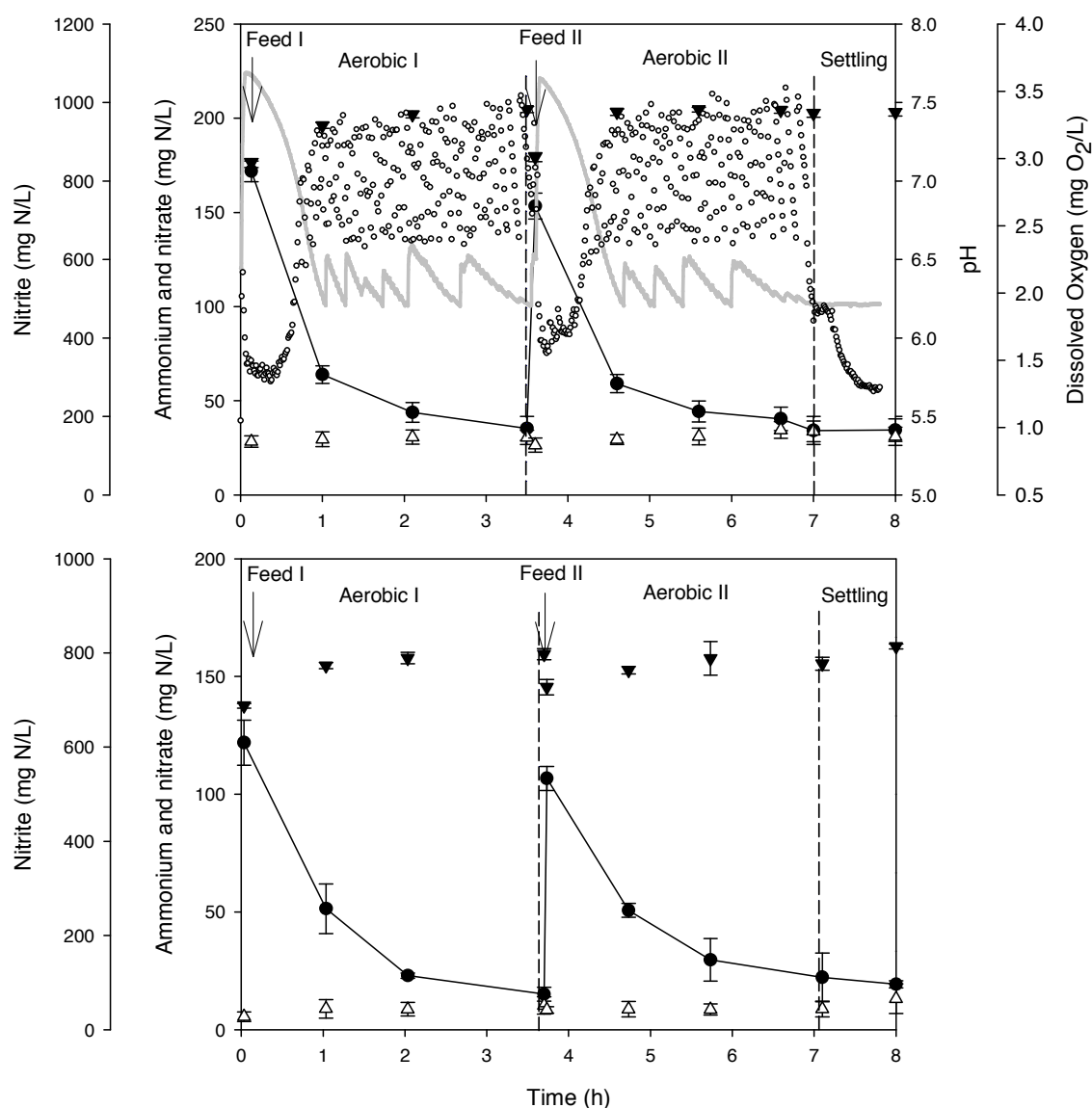


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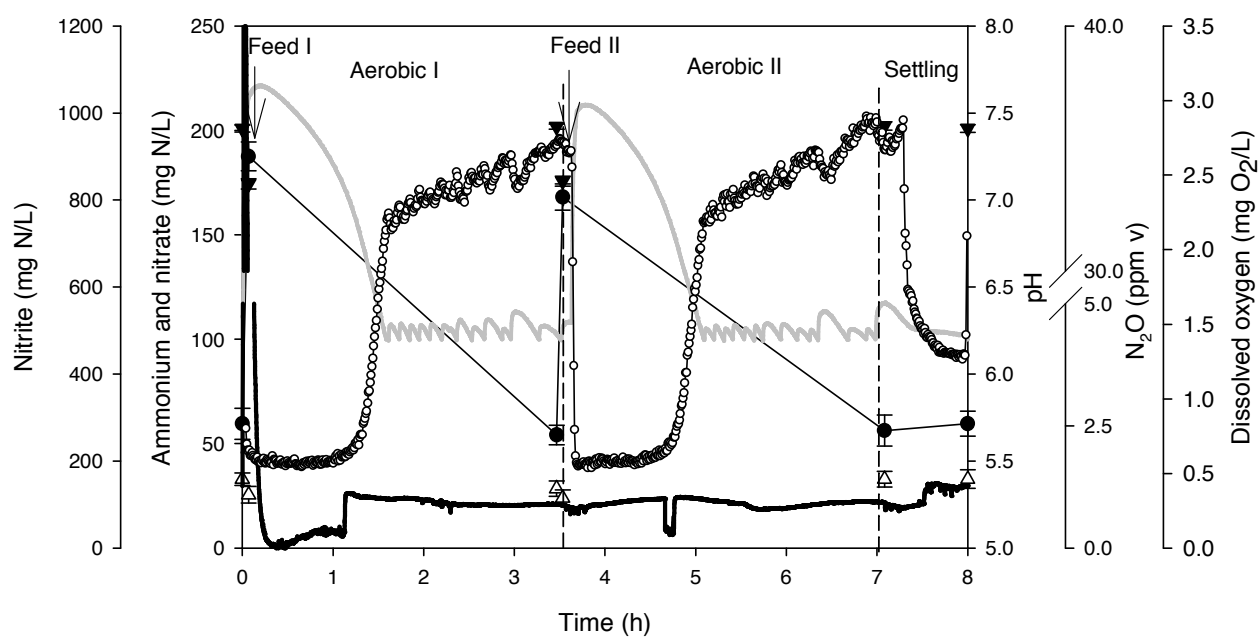


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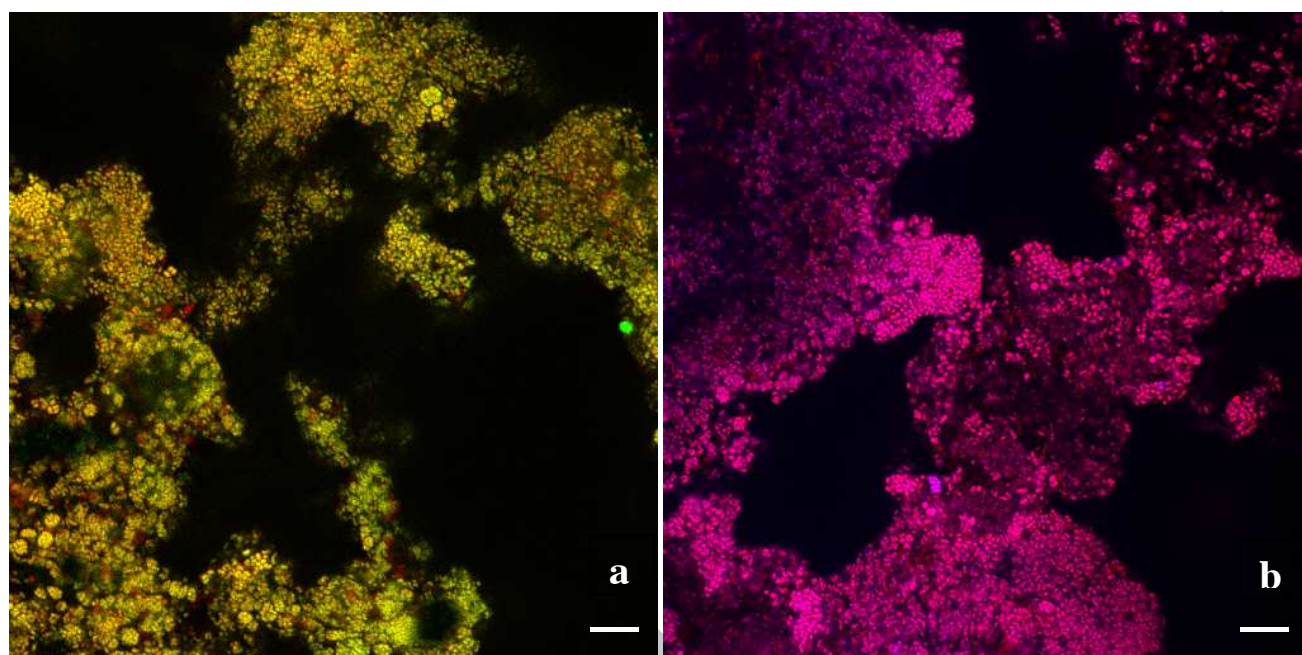


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Highlights

- Free nitrous acid (FNA) is produced from anaerobic digestion liquor (DL).
- Complete nitrification of the DL is achieved with online pH controller.
- Nitrite in the treated DL required minimal acid for its conversion to FNA.
- Only 0.08% of N converted was emitted as nitrous oxide.